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# Kinetic and Thermodynamic Stability of Acenes: Theoretical Study of Nucleophilic and Electrophilic Addition

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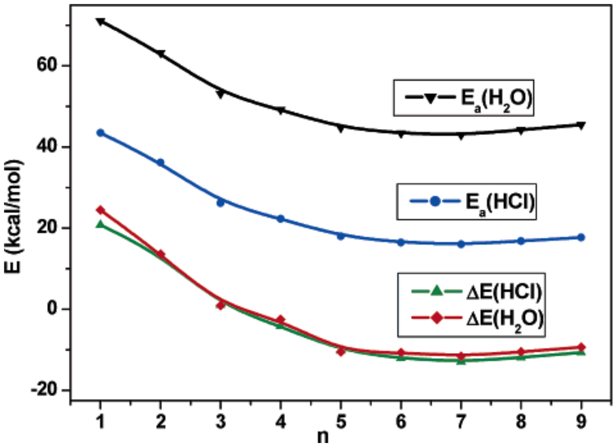
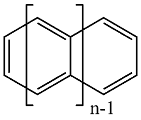


To understand the reactivity of acenes, particularly pentacene, the addition of HCl and water to acenes was studied for the benzene−nonacene series at the B3LYP/6-31G(d) level of theory. Surprisingly, the reactivity of the acenes increases along the series up to hexacene and remains constant from hexacene and above due to the biradical character of the ground state of higher acenes. While the exothermicity of HCl and water additions are very similar, the activation barriers for HCl and water additions differ by a constant factor of ca. 27 kcal/mol. The barrier for the addition of HCl varies from 44 kcal/mol for benzene to 16−18 kcal/mol for pentacene−nonacene, whereas the barrier for the addition of water varies from 71 kcal/mol for benzene to 43−46 kcal/mol for pentacene−nonacene. The transition states (TSs) for the addition of water to acenes are relatively “late” on the reaction coordinate, compared to the “earlier” TSs for the addition of HCl. There is a substantial substituent effect on the energy barriers for these reactions. HCl behaves as an electrophile, with $\rho_{HCl}$ (vs $\sigma_p$) = −4.48 and −3.39 for anthracenes and pentacenes, respectively, while water behaves as a nucleophile, with $\rho_{H_2O}$ (vs $\sigma_p$) = 2.35 and 1.39 for anthracenes and pentacenes, respectively.

## Introduction

Acenes (**I**) are polycyclic aromatic hydrocarbons (PAHs)



**(I)**

consisting of linearly fused benzene rings. In the recent past, these substances have been of interest from fundamental and applied perspectives.[1,2] Smaller acenes, such as benzene, naphthalene, and anthracene, are among the earliest discovered and most studied organic compounds and their properties are well explored. Electrophilic substitutions on these molecules are the most common reactions.[3] Nucleophilic substitution onto acenes is much more rare and occurs only in extreme cases of strongly activated acenes.[3] Yet, very little is known about the

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10.1021/jo061552o CCC: $37.00

reactivity of acenes above anthracene, such as tetracene, pentacene, and higher acenes. Among the existing acenes, pentacene has received considerable attention in the recent past as the most promising active semiconductor for use in organic field effect transistors (FET) because of its high charge-carrier mobility; however, poor environmental stability is one of the problems limiting its practical application.[4] Homologues longer than hexacene have not been fully characterized and the synthesis of heptacene remains controversial,[5] although heptacene substituted by bulky protecting groups has been synthesized recently.[6] As the number of rings increases, the members of the acene family become increasingly reactive.[7−9] The central ring of anthracene undergoes Diels−Alder reactions,[1a−c,7] protonation,[9] and other reactions, while very few reactions have been reported for tetracenes and pentacenes.[10,11,12]

The electronic properties of large acenes have been examined theoretically by many groups. Despite large strides in the sophistication of the theoretical treatments used over the last 30 years, the HOMO−LUMO gap, electronic structure, stability/reactivity, and aromaticity of an acene or polyacene are still subjects of controversy.[13−16] A successive reduction in the band gap[17] and ionization potential,[18] and an increase in proton[9] and electron affinities[19] is observed along the acene series. Such progressions in acene properties appear to coincide with the sequential loss of benzenoid character (aromaticity) predicted by early MO treatments and Clar's qualitative sextet concept.[20] Recently, longer acenes were predicted to be biradical singlets in the ground state due to their disjointed nonbonding molecular orbitals.[16]

Schleyer et al. have theoretically studied aromaticity and the Diels−Alder reactions of acenes with acetylene.[14c] Surprisingly, they found that there is no significant decrease in relative aromatic stabilization based on nucleus-independent shift (NICS)[21] estimations.[14c] It has also been predicted that the more reactive inner rings are actually more aromatic than the less reactive outer rings, and that they are even more aromatic than benzene itself.[22] At the same time, the HOMO coefficients are consistent with the regioselectivity of Diels−Alder reactions that prefer the middle rings (despite their greater aromaticity).[14c] The reaction mechanism for the addition of oxygen to acenes has been studied theoretically.[23] It was found that, starting from anthracene, acenes react with oxygen via a biradical stepwise mechanism.[23] The reactions of the acene series have not been studied theoretically except for the two examples mentioned above, namely the Diels−Alder reaction with acetylene[14c] and the addition of oxygen to acenes.[23]

To understand the stability and reactivity of the acenes, in particular higher acenes, we have theoretically studied the mechanism by which nucleophilic and electrophilic additions take place, using HCl and water as a model electrophile and nucleophile, respectively. Here we report the first systematic theoretical study of the potential energy surfaces for the addition of HCl and water to the acenes (Scheme 1). We have chosen the following acenes (Figure 1): benzene (**1**), naphthalene (**2**), anthracene (**3**), tetracene (**4**), pentacene (**5**), hexacene (**6**), heptacene (**7**), octacene (**8**), and nonacene (**9**). Benzenes (**1-CN**, **1-F**, **1-OMe**), anthracenes (**3-CN**, **3-F**, **3-OMe**), and pentacenes (**5-CN**, **5-F**, **5-OMe**) substituted by four cyano (n-CN), four fluoro (n-F) or four methoxy groups (n-OMe) were also studied (Scheme 2). We found that the kinetic and the thermodynamic stability of acenes decreases from benzene to hexacene and then stays constant for the longer acenes due to their biradical ground state.

## Computational Methods

The Gaussian 03[24] series of programs was used for all calculations. All molecules were fully optimized by using the hybrid density functional[25] B3LYP level[26] of theory with the 6-31G(d) basis set (denoted as B3LYP/6-31G(d)). The relative energies included unscaled zero point vibrational energies (ZPVE). All

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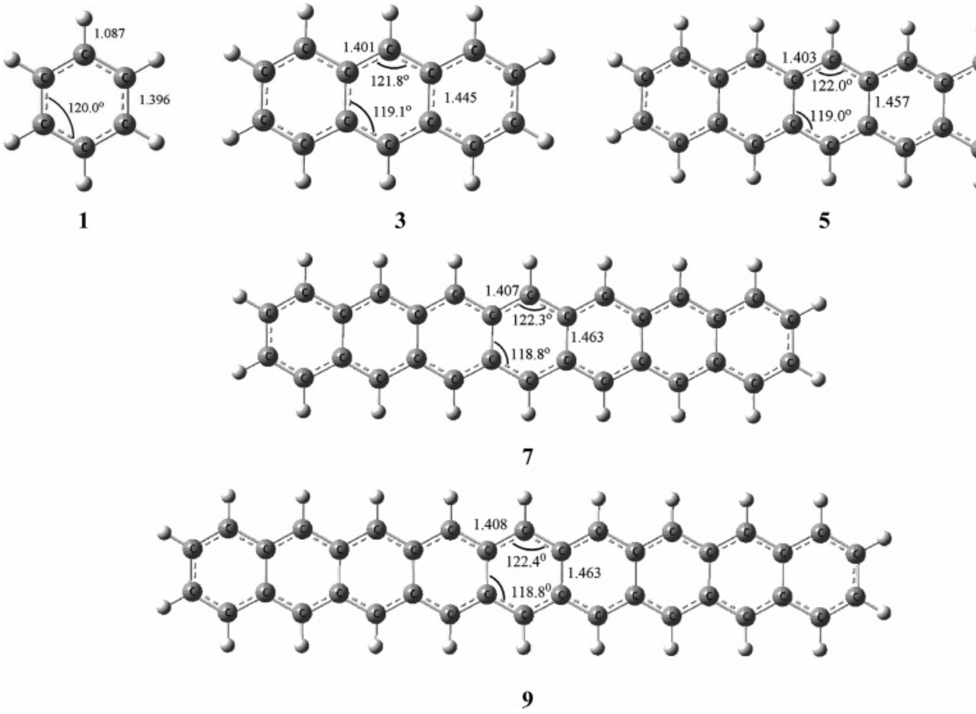
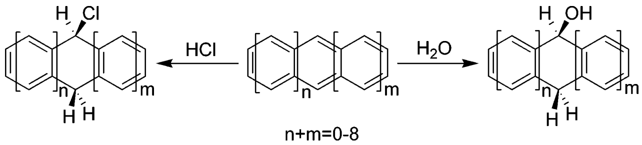


**FIGURE 1.** Optimized structures of benzene (**1**), anthracene (**3**), pentacene (**5**), heptacene (**7**), and nonacene (**9**) at the B3LYP/6-31G(d) level of theory (bond angles in deg and bond lengths in Å; heptacene and nonacene are calculated at UB3LYP/6-31G(d)).

**SCHEME 1**



results reported in this paper are at the B3LYP/6-31G(d)+ZPVE level of theory unless stated otherwise. For discussion of the benchmark results at different theoretical levels see the Supporting Information. We note that in contrast to many ab initio methods (such as MP2, CISD, CCSD, etc.) the B3LYP level always yields real frequencies for benzene regardless of the basis set used.[27] Transition structures were located by using the TS routine as implemented in Guassian 03. Frequency calculations were performed at the same level for all stationary points to differentiate them as minima or saddle points. Intrinsic Reaction Coordinate (IRC)[28] calculations were performed for several representative cases. Charge distribution was estimated by using Mulliken population analysis at B3LYP/6-31G(d). In some cases charges from natural population analysis (NPA charges)[29] were also calculated at B3LYP/6-31G(d) and compared to the Mulliken charges.

No attempts have been made to locate all possible complexes between HCl or water and acenes. Basis set superposition errors (BSSE) were estimated by using the counterpoise corrections method for HCl and water complexes with acenes.[30] The addition of HCl or water has been studied only with respect to the central acene ring, since it is known to be the most reactive.[1-3,8,10] The wave function of the ground state of molecules **6**−**9** includes a contribution from the singlet biradical state due to the disjoint biradical nature of the ground state.[16] Thus, we have considered the reactions of molecules **6**−**9** at UB3LYP/6-31G(d) unless stated otherwise.

Throughout the paper, on the central benzene ring, $C_\alpha$ refers to the carbon that adds Cl or O (from HCl or water, respectively), and $C_\beta$ refers to the carbon that adds hydrogen. In the case of the addition of water, the hydrogen that is added to the acene skeleton is marked $H^1$, and the hydrogen that remains bonded to oxygen is marked $H^2$. We will call addition "nucleophilic" in cases where acene acts as an electrophile and the second reactant acts as a nucleophile, and we will call addition "electrophilic" in cases where acene acts as a nucleophile and the second reactant acts as an electrophile.

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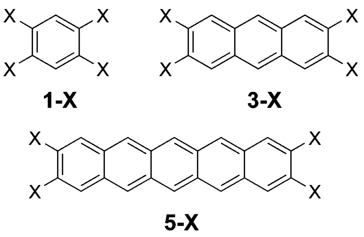
**SCHEME 2**



X = CN, F, H, OMe

**SCHEME 3: 1,2- and 1,4-Addition of HCl or Water to Benzene**

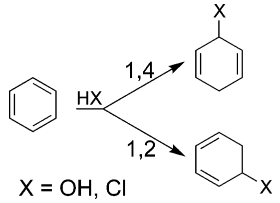


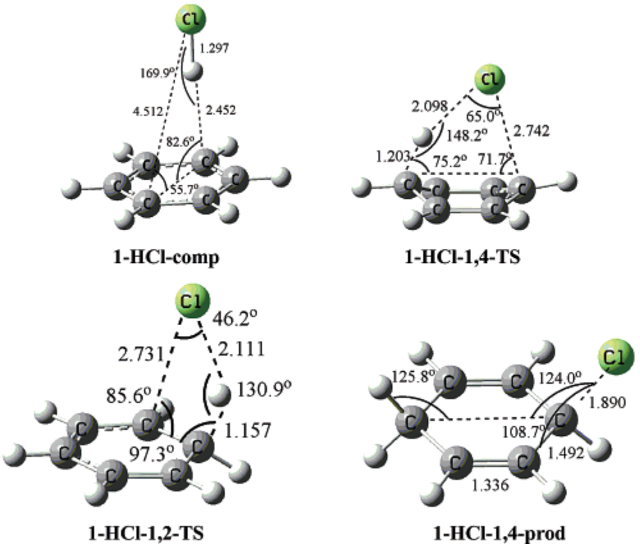
**TABLE 1: Calculated Activation ($\Delta E_a$) and Product ($\Delta E$) Energies (in kcal/mol, at B3LYP/6-31G(d)+ZPVE) for the Addition of HCl or Water to Ethylene and to the 1,4- and 1,2-Positions of Benzene**

| | transition state ($\Delta E_a$) | | product ($\Delta E$) | |
|---|---|---|---|---|
| | HCl | water | HCl | water |
| $H_2C{=}CH_2$ | 33.7 | 48.1 | −21.3 | −18.7 |
| benzene (1,4) | 43.5 | 71.1 | 20.8 | 24.5 |
| benzene (1,2) | 41.9 | 63.9 | 20.2 | 23.3 |

## Results and Discussions

**I. Addition of HCl or Water to Benzene.** Benzene can react with HCl or water via a 1,2- or 1,4-addition mechanism (Scheme 3). Since addition of HCl or water to acenes occurs at the 1,4-position of the central ring, we will mostly discuss 1,4-addition of HCl or water to benzene, although 1,2-addition is both kinetically and thermodynamically preferable over 1,4-addition, due to the presence of the conjugated double bonds in 1,2-addition products. The reaction mechanism for addition of HCl or water to benzene proceeds via formation of a benzene−HCl or benzene−water complex followed by a transition state that leads to the addition product. Complexes between HCl or water and benzene have been studied extensively previously[31] and will be discussed here only briefly.

We have compared the addition of HCl or water to benzene with their respective additions to ethylene (Table 1). Activation barriers for addition of both HCl and water to ethylene (33.7 and 48.1 kcal/mol, respectively) are significantly lower than those for addition to benzene (at both the 1,2 and 1,4 positions). We note that the difference in the reactivity of benzene toward HCl compared to water is significant (71.1 − 43.5 = 27.6 kcal/mol for 1,4-addition and 63.9 − 41.9 = 22.0 kcal/mol for 1,2-addition), while the difference in the reactivity of ethylene toward HCl compared to water is smaller (48.1 − 33.7 = 14.4 kcal/mol). We believe that the reason for this difference is that the electrophilic addition to benzene is known as a common reaction (and HCl acts as an electrophile) while nucleophilic addition to benzene is an uncommon reaction for benzene (and water acts as a nucleophile); i.e., benzene is a better nucleophile than electrophile.



**1-HCl-comp** **1-HCl-1,4-TS** **1-HCl-1,2-TS** **1-HCl-1,4-prod**

**FIGURE 2.** Optimized structures for the reaction of benzene with HCl: the benzene−HCl complex, the 1,4- and 1,2-addition transition states, and the 1,4-addition product at the B3LYP/6-31G(d) level of theory (bond angles in deg and bond lengths in Å).

**TABLE 2: The Complexation ($\Delta E$) and Gibbs Free ($\Delta G°$) Energies (Relative to HCl or Water and Acene) of Complexes of Acenes with HCl or Water (kcal/mol, at B3LYP/6-31G(d)+ZPVE, the BSSE Corrected Energies Are Shown in Parentheses)**

| | HCl | | water | |
|---|---|---|---|---|
| acene | $\Delta E$ | $\Delta G°$ | $\Delta E$ | $\Delta G°$ |
| **1** | −2.1 (−1.5) | 2.4 | −2.0 (−0.5) | 3.2 |
| **2** | −2.0 (−1.4) | 4.5 | −1.9 (−0.6) | 3.7 |
| **3** | −1.7 (−1.1) | 5.0 | −1.7 (−0.3) | 4.0 |
| **4** | −1.7 (−1.1) | 3.9 | −1.6 (−0.2) | 3.6 |
| **5** | −1.7 (−1.1) | 4.3 | −1.5 (−0.1) | 4.1 |

**1. Addition of HCl to Benzene.** The 1,4-addition of HCl to benzene poses an energy barrier of 43.5 kcal/mol (Table 1) (activation free energy is 51.5 kcal/mol, see Table 4). The 1,2-addition of HCl to benzene has a slightly lower activation energy of 41.9 kcal/mol. The calculated structures of the benzene HCl complex (**1-HCl-comp**), of both the 1,4- and 1,2-addition transition states (**1-HCl-1,4-TS** and **1-HCl-1,2-TS**), and of the 1,4-addition product (**1-HCl-1,4-prod**) are shown in Figure 2.

In the first step of the addition reaction, HCl forms a weak complex, **1-HCl-comp**, with benzene.[32] The relative energy of the complex (Table 2) is negative (−2.1 kcal/mol; −1.5 kcal/mol after BSSE correction), while the free energy of the complex

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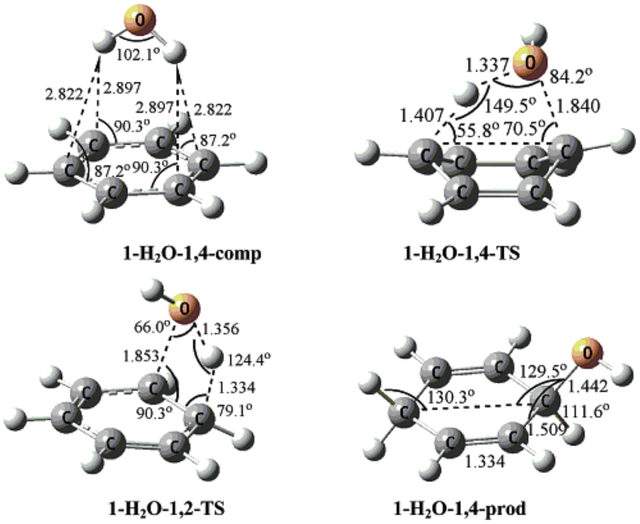
(32) When aromatic hydrocarbons are treated with HCl alone, $\pi$ complexes are formed. The use of HCl plus a Lewis acid (e.g., $AlCl_3$) gives arenium ions. The two types of solution have very different properties. For example, a solution of an arenium ion is colored and conducts electricity, while a $\pi$ complex formed from HCl and benzene is colorless and does not conduct a current. Furthermore, when DCl is used to form a $\pi$ complex, no deuterium exchange takes place, while formation of an arenium ion with DCl and $AlCl_3$ gives deuterium exchange. See p 679 in ref 3.



**1-H$_2$O-1,4-comp** **1-H$_2$O-1,4-TS**

**1-H$_2$O-1,2-TS** **1-H$_2$O-1,4-prod**

**FIGURE 3.** Optimized structures for the reaction of benzene with water: the 1,4-addition complex, both the 1,2- and 1,4-addition transition states, and the 1,4-addition product at the B3LYP/6-31G(d) level of theory (bond angles in deg and bond lengths in Å).

is positive (2.4 kcal/mol). The C−C bonds are elongated by ≤0.003 Å (up to a length of 1.399 Å), relative to the isolated benzene, and the distortion of the C−C−C angles from 120° is negligible (≤0.03°). The complex has $C_s$ symmetry. From the complex, addition of HCl proceeds to product, **1-HCl-1,4-prod** (shown) or **1-HCl-1,2-prod** (not shown), via one of the electrophilic transition states, **1-HCl-1,4-TS** or **1-HCl-1,2-TS**, respectively, in which chlorine attacks the carbon atom of benzene. In the transition state, benzene is bent (the sums of the angles around $C_1$ and $C_4$ are 358.7° and 349.7°, respectively, in **1-HCl-1,4-TS**). The $C_1$−Cl bond distance in the TS is relatively long (2.742 Å in **1-HCl-1,4-TS**, relative to 1.890 Å in **1-HCl-1,4-prod**). For 1,4-addition, the TS has $C_s$ symmetry. The negative eigenvector of those transition states includes mostly proton transfer from HCl to the benzene carbon atom, which indicates that the transition states are electrophilic.

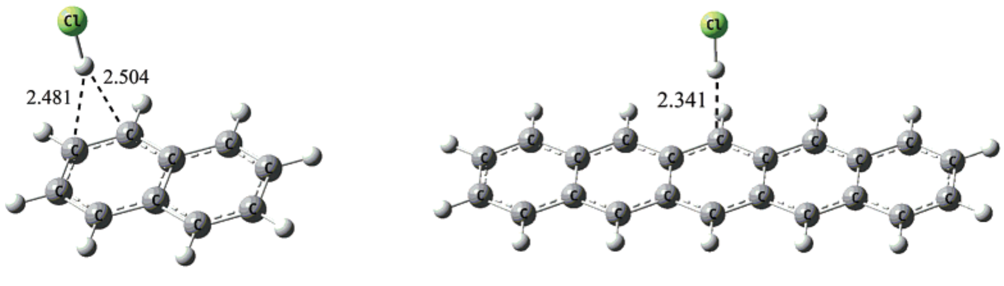
**2. Addition of Water to Benzene.** Although benzene does not react with water in the absence of a catalyst under reasonable experimental conditions,[32] we have studied this reaction theoretically to compare longer acenes with benzene. The calculated structures of the 1,4-addition benzene−water complex (**1-H$_2$O-1,4-comp**), both the 1,4- and 1,2-addition transition states (**1-H$_2$O-1,4-TS** and **1-H$_2$O-1,2-TS**), and the 1,4-addition product (**1-H$_2$O-1,4-prod)** are shown in Figure 3. Addition of water to benzene poses a very high activation barrier of 71.1 kcal/mol (the activation free energy is 79.8 kcal/mol, Table 5) for 1,4-addition and 63.9 kcal/mol for 1,2-addition (Table 1) as expected[3] for nucleophilic addition to benzene.

In the first step of the addition reaction, water forms a weak complex, **1-H$_2$O-1,4-comp**, with benzene. The relative energy (Table 2) of **1-H$_2$O-1,4-comp** is negative (−2.0 kcal/mol; −0.5 kcal/mol after BSSE correction) and the free energy of the complex (3.2 kcal/mol) is positive. The C−C bonds are elongated by only ≤0.002 Å, relative to the isolated benzene, and the distortion of the C−C−C angles from 120° is negligible (≤0.02°). The complex has $C_2$ symmetry. The transition states, **1-H$_2$O-1,4-TS** and **1-H$_2$O-1,2-TS**, for the addition of water to benzene have both electrophilic and nucleophilic contributions (Figure 3), and lead to the formation of the corresponding products. In **1-H$_2$O-1,4-TS**, carbon atoms $C_1$ and $C_4$ are pyramidalized (the sum of the angles around $C_1$ and $C_4$ is 351.1° and 351.2°, respectively), the $C_1$−O bond length is relatively long (1.840 Å) compared to that of **1-H$_2$O-1,4-prod** (1.442 Å), and the $C_1$−$C_2$ bond is also significantly elongated (1.456 Å in **1-H$_2$O-1,4-TS**) relative to that of benzene (1.396 Å). The $C_1$−$C_2$ bond in **1-H$_2$O-1,4-prod** is 1.509 Å. Bond lengths and bond angles in **1-H$_2$O-1,2-TS** are similar to those in **1-H$_2$O-1,4-TS** (Figure 3). Thus, **1-H$_2$O-1,4-TS** and **1-H$_2$O-1,2-TS** can be characterized as being "late" transition states along the reaction coordinate.

Thus, the transition state for addition of water to benzene is "later" than the transition state for addition of HCl to benzene, and the activation energy for addition of water is significantly higher than that for the addition of HCl, although the activation energy for the latter is high in the gas phase. Inclusion of solvent effects lowers the activation barriers.[33] We also note that Cl is better able to stabilize negative charge than OH, thus HCl acts as an electrophile, while water acts as a nucleophile in reactions with acenes.

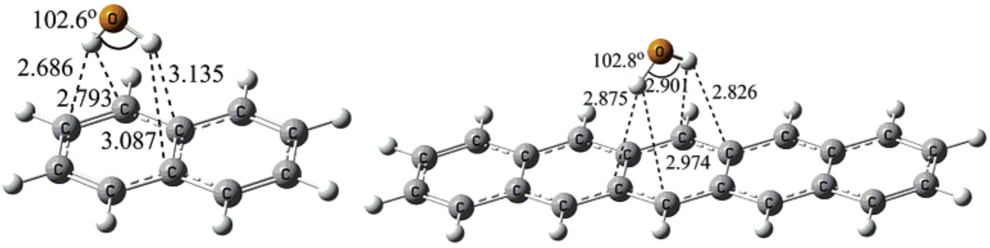
**II. Addition of HCl or Water to Acenes.** We expect the addition of HCl or water to higher acenes to proceed by a mechanism like that for benzene, i.e., via a single transition state that leads to the corresponding product. The acenes studied are benzene (**1**), naphthalene (**2**), anthracene (**3**), tetracene (**4**), pentacene (**5**), hexacene (**6**), heptacene (**7**), octacene (**8**), and nonacene (**9**). Figure 1 shows the representative B3LYP/6-31G(d) optimized geometries of acenes.

**1. Complex Formation.** We found several weakly bound complexes between HCl or water and acenes.[34] The calculated geometries of some HCl and water complexes with acenes are presented in Figures 4 and 5, respectively. The complexes of HCl with **2**, **3**, **4**, and **5** are 2.0, 1.7, 1.7, and 1.7 kcal/mol more



**2-HCl-comp** **5-HCl-comp**

**FIGURE 4.** Representative optimized structures of complexes of HCl with naphthalene and pentacene at the B3LYP/6-31G(d) level of theory (bond lengths in Å).



**2-$H_2O$-comp** **5-$H_2O$-comp**

**FIGURE 5.** Representative optimized structure of complexes of water with naphthalene and pentacene at the B3LYP/6-31G(d) level of theory (bond angles in deg and bond lengths in Å).

**TABLE 3: Mulliken Charges for the Transition States (TS) for HCl and Water Additions to Acenes at B3LYP/6-31G(d)[a]**

| | Mulliken charges (e) | | | | | |
|---|---|---|---|---|---|---|
| | HCl | | $H_2O$ | | | |
| acene + HCl/$H_2O$ | H | Cl | $H^1$ | O | $H^2$ | $OH^2$ |
| **1−1,4-TS** | 0.26 [0.34] | −0.53 [−0.57] | 0.35 [0.43] | −0.69 [−0.81] | 0.38 [0.47] | −0.30 [−0.34] |
| **2-TS** | 0.25 | −0.54 | 0.36 | −0.69 | 0.39 | −0.30 |
| **3-TS** | 0.25 | −0.57 | 0.37 | −0.68 | 0.40 | −0.28 |
| **4-TS** | 0.24 | −0.58 | 0.37 | −0.68 | 0.40 | −0.28 |
| **5-TS** | 0.24 | −0.60 | 0.37 | −0.68 | 0.41 | −0.27 |
| **6-TS** | 0.24 (0.24) | −0.58 (−0.60) | 0.38 | −0.67 | 0.41 | −0.26 |
| **7-TS** | 0.24 (0.23) | −0.57 (−0.60) | 0.38 | −0.67 | 0.41 | −0.26 |
| **8-TS** | 0.24 (0.23) | −0.55 (−0.61) | 0.38 | −0.67 | 0.41 | −0.25 |
| **9-TS** | 0.24 (0.23) | −0.55 (−0.61) | 0.38 | −0.66 | 0.41 | −0.25 |

[a] Charges from natural population analysis (NPA)[29] are shown in square brackets. (For **6-HCl-TS**, **7-HCl-TS**, **8-HCl-TS**, and **9-HCl-TS**, the values are at UB3LYP/6-31G(d), and the RB3LYP/6-31G(d) values are given in parentheses.) In the HCl isolated molecule, the charges on hydrogen and on chlorine are 0.23*e* and −0.23*e*, respectively. In the isolated water molecule, the charges on H and O are 0.39*e* and −0.77*e*, respectively.

stable than the reactants (Table 2). The stability of these complexes decreases to 1.1−1.4 kcal/mol after inclusion of basis set superposition errors (BSSE). This is similar to findings for the HCl complex with benzene (**1-HCl-comp**), which is 2.1 kcal/mol more stable than the reactants (1.5 kcal/mol more stable than the reactants after inclusion of BSSE), Table 2. In the case of water complexes with acenes, the complexation energies after inclusion of BSSE are very small (Table 2). The **2-$H_2O$-comp** and **5-$H_2O$-comp** are more stable than the reactants by 1.9 and 1.5 kcal/mol, respectively (0.6 and 0.1 kcal/mol, respectively, after inclusion of BSSE), which is similar to **1-$H_2O$-1,4-comp**, which is by 2.0 kcal/mol more stable than the reactants (Table 2 and Figure 5). Thus, all water−acene complexes can be described as very weak. The free energies of all complexes are positive. The $C_\beta \cdots H$ distances are 2.452, 2.504, 2.379, 2.366, and 2.341 Å for **1-HCl-comp**, **2-HCl-comp**, **3-HCl-comp**, **4-HCl-comp**, and **5-HCl-comp**, respectively. The $C_\beta \cdots H^1$ distances are 2.822, 2.793, and 2.802 Å for **1-$H_2O$-1,4-comp**, **2-$H_2O$-comp**, and **3-$H_2O$-comp**, respectively. Overall, we expect that these complexes will not play an important role in HCl or water addition to acenes.

**2. Charge Distribution in the Transition States for Addition of HCl or Water to Acenes.** The Mulliken charges for the transition states for addition of HCl or water to acenes are summarized in Table 3. In the transition states for HCl addition to acenes, the charge on hydrogen is similar to the charge on hydrogen in the isolated HCl molecule (0.23*e*). It very slightly decreases across the transition states from benzene (0.26*e*) to tetracene (0.24*e*), and then remains constant at this value for longer acenes. The absolute value of the charge on chlorine (actual charges: −0.53 to −0.60*e*) in these transition states is much larger than the absolute value of the charge on chlorine in isolated HCl (actual charge: −0.23*e*). The absolute values slightly increase from benzene (actual charge: −0.53*e*) to pentacene (actual charge: −0.60*e*), before decreasing from pentacene to nonacene (actual charge: −0.55*e*). The charges on the H and Cl atoms that originated from HCl and that are transferred to the products (for example, 0.17*e* on H and −0.13*e* on Cl in **1-HCl-1,4-prod**, and 0.20*e* on H and −0.12*e* on Cl in **9-HCl-prod**) are much smaller than the charges on these atoms in the isolated HCl molecule or in the transition states, which indicates that the transition states are relatively polar. Thus, overall, the charge on the H and Cl atoms that originates from HCl increases from the reactants to the transition states, before decreasing in the products.

A different charge distribution behavior is observed for the transition states for the addition of water to acenes (Table 3). The polarity of all the transition states for water addition is very similar and is similar to the charge distribution observed in the isolated water molecule (0.39*e* on hydrogen, −0.77*e* on oxygen). The charges on the $H^1$ and $OH^2$ group in the products (for example, 0.16*e* on $H^1$ and −0.24*e* on $OH^2$ in **1-$H_2O$-1,4-prod**, and 0.19*e* on $H^1$ and −0.23*e* on $OH^2$ in **9-$H_2O$-prod**) are much smaller than the charges on the $H^1$ and $OH^2$ part of the isolated water molecule and in the transition states. Thus, also in the case of water addition, the transition states are relatively polar.

Generally, the differences in charge distribution between HCl and water additions can be explained by the different nature of

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(33) Calculated results for addition of HCl and water to acenes in different solvents with use of PCM model are given in the Supporting Information.

(34) These complexes do not necessarily comprise all possible complexes between HCl or water and acenes.

**TABLE 4: Calculated Activation Energies ($\Delta E_a$), Activation Free Energies ($\Delta G^{\ddagger}$), Product Energies ($\Delta E$), and Product Free Energies ($\Delta G^{\circ}$) (kcal/mol, at B3LYP/6-31G(d)+ZPVE, Relative to HCl and Acene, Free Energies are Calculated at 298 K) for the Addition of HCl to Acenes**[a]

| | transition state | | product | |
|---|---|---|---|---|
| acene | $\Delta E_a$ | $\Delta G^{\neq}$ | $\Delta E$ | $\Delta G^{\circ}$ |
| **1−1,4** | 43.5 | 51.5 | 20.8 | 28.4 |
| **2** | 36.2 | 45.7 | 13.4 | 22.4 |
| **3** | 26.2 | 35.6 | 1.0 | 10.3 |
| **4** | 22.3 | 30.8 | −4.2 | 4.3 |
| **5** | 18.0 | 26.9 | −10.2 | −1.2 |
| **6** | 16.5 (15.8) | 25.5 (24.2) | −12.1 (−12.9) | −2.7 (−4.3) |
| **7** | 16.0 (13.5) | 24.1 (21.9) | −12.9 (−15.7) | −4.3 (−7.1) |
| **8** | 16.8 (12.2) | 25.7 (21.4) | −11.9 (−17.1) | −2.5 (−7.8) |
| **9** | 17.8 (10.9) | 26.6 (19.2) | −10.7 (−18.5) | −1.3 (−10.0) |

[a] Reactions involving **6**−**9** were calculated at UB3LYP/6-31G(d) (the RB3LYP/6-31G(d) values are given in parentheses).

these reactions. Addition of HCl is electrophilic, and indeed, in transition states, a significant amount of charge (ca. 0.30−0.35*e*) is transferred from acene to HCl moiety; addition of water is nucleophilic, and in the transition state, charge (ca. 0.1*e*) is transferred from water to acene.

**3. Activation Energies for the Addition of HCl to Acenes.**[33] The calculated relative energies for the addition of HCl to acenes **1**−**9** are given in Table 4. The restricted (R) wave function for the transition states of **6-HCl-TS-R** through to **9-HCl-TS-R** shows RHF → UHF instability, thus those structures were reoptimized by using an unrestricted (U) DFT at UB3LYP/6-31G(d). Reactions of HCl with benzene (**1**), naphthalene (**2**), and anthracene (**3**) are endothermic while the reactions with higher acenes are exothermic. It is well recognized[1,3] that the reactivity of acenes increases with the number of benzene rings and stability of the addition products also increases with the number of benzene rings. The Clar aromatic sextet valence bond model[1a] is usually used to explain this phenomenon. With lower members of the acene series, the activation barriers for addition of HCl are relatively high (for example, 36.2 kcal/mol for naphthalene) and the reaction is not expected to proceed at room temperature. As the number of benzene rings increases, the activation energy decreases from benzene (43.5 kcal/mol) to hexacene (16.5 kcal/mol), and then remains almost constant from hexacene to nonacene (17.8 kcal/mol), at UB3LYP/6-31G(d) (Table 4, Figure 6).[35] Thus, we can expect longer acenes to react with HCl at room temperature in solution or in the gas phase. We note that in the solid state (as crystals or in ordered films, for example, in the pentacene film used in FETs) the reactions may exhibit higher activation barriers because the planar structure of acenes needs to bend to form the structure of the HCl−acene addition product. If the RB3LYP/6-31G(d) values are considered, then as the number of benzene rings increases, the activation energy decreases continuously from benzene (43.5 kcal/mol) to nonacene (10.9 kcal/mol, Table 4, Figure 6). The activation energies for the transition states for HCl addition to acenes **6**−**9** calculated at UB3LYP are generally higher than those at the RB3LYP level due to lower energies of the reactants (acenes) at the UB3LYP level compared to the RB3LYP level. For a detailed discussion of electronic structure of acenes **6**−**9** see ref 16.

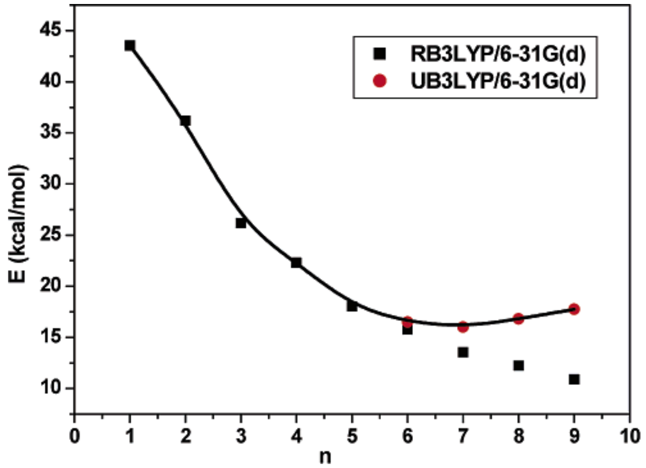

**FIGURE 6.** Activation energies for the addition of HCl to acenes, plotted as a function of annellation: (black square) at RB3LYP/6-31G-(d) and (red circle) at UB3LYP/6-31G(d).

Representative transition state structures for the addition of HCl to acenes are shown in Figure 7. All geometries entail four-centered structures involving the $C_\alpha$ and $C_\beta$ of benzene, and the chlorine and hydrogen atoms of the HCl molecule. These four atoms are nearly in the same plane (the largest H−Cl−$C_\alpha$−$C_\beta$ dihedral angle is 1.2° for **2-HCl-TS**, while acenes with an odd number of benzene rings present a 0° dihedral angle). In the TSs (shown in Figure 7), $C_\beta\cdots H$ bond formation is nearly complete while the $C_\alpha\cdots Cl$ bond is not yet formed.[36,37] The $C_\alpha$−Cl bond length increases significantly from **1-HCl-TS** (2.742 Å) to **9-HCl-TS** (4.184 Å), while the H−Cl bond length decreases from **1-HCl-TS** (2.098 Å) to **9-HCl-TS** (2.055 Å). Thus, the transition state for HCl addition to acenes is relatively "late" on the reaction coordinate, while as the number of benzene rings increases along the acenes series, the transition state moves slightly "earlier" on the reaction coordinate. The $C_\beta\cdots H$ bond length decreases slightly (from 1.203 Å for **1-HCl-TS** to 1.145 Å for **9-HCl-TS**) along the acene series. The direction of the eigenvector shows that in **1-HCl-TS**, the hydrogen of HCl moves the most, and the Cl atom is almost motionless. The contribution of the Cl atom to the motion increases as the number of benzene rings increases, and for the higher acenes, such as octacene and nonacene, the motion is mostly of the Cl atom and much less of the hydrogen.

**4. Activation Energies for the Addition of Water to Acenes.** The calculated relative energies at the B3LYP/6-31G-(d) level for the addition of water to acenes **1**−**9** are given in Table 5. The activation energies for addition of water to acenes are very large (Table 5). The activation barrier for the addition of water to benzene is 71.1 kcal/mol, which decreases to 43.0−

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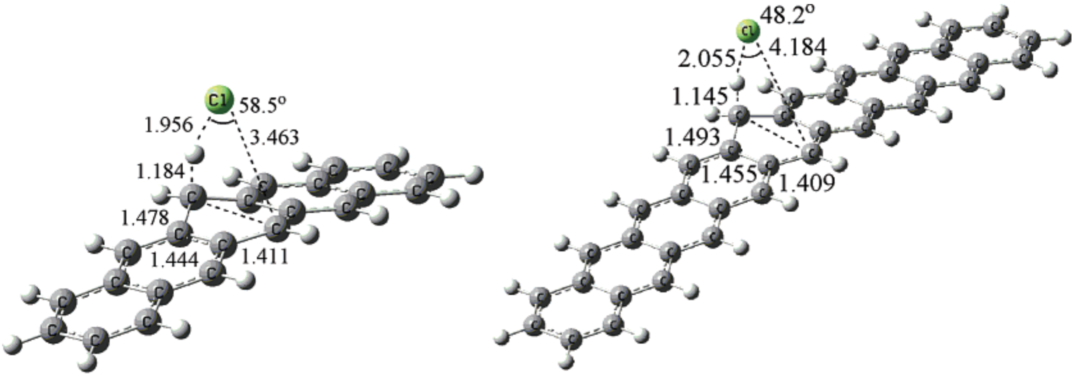
(35) The spin contamination ($S^2$) of these TSs ($S^2$ of corresponding acenes are given in parantheses)[16] are 0.15 (0.26), 0.28 (0.80), 0.37 (1.08), and 0.43 (1.26) respectively for hexacene, heptacene, octacene, and nonacene. Thus, the $S^2$ values for transition states are smaller than those for the corresponding acenes,[16] which is due to the partial deformation from planarity in acene backbone that occurs in the transition state, which destabilizes the disjoint biradical structure and generates a preference for the closed shell state.

(36) The $C_\beta\cdots H$ ($C_\alpha\cdots Cl$) distances in the transition states are the following: 1.203 Å (2.742 Å) in **1-HCl-1,4-TS**, 1.201 Å (2.872 Å) in **2-HCl-TS**, 1.193 Å (3.110 Å) in **3-HCl-TS**, 1.189 Å (3.256 Å) in **4-HCl-TS**, 1.184 Å (3.463 Å) in **5-HCl-TS**, 1.166 Å (3.689 Å) in **6-HCl-TS**, 1.155 Å (3.932 Å) in **7-HCl-TS**, 1.150 Å (4.055 Å) in **8-HCl-TS**, and 1.145 Å (4.184 Å) in **9-HCl-TS**. The data for reactions which involve acenes **6**−**9** are at UB3LYP/6-31G(d).

(37) $C_\beta\cdots H$ ($C_\alpha\cdots Cl$) distances at RB3LYP/6-31G(d) are the following: 1.182 Å (3.613 Å) in **6-HCl-TS-R**, 1.180 Å (3.815 Å) in **7-HCl-TS-R**, 1.178 Å (3.974 Å) in **8-HCl-TS-R**, and 1.175 Å (4.168 Å) in **9-HCl-TS-R**.



**5-HCl-TS** **9-HCl-TS**

**FIGURE 7.** Representative optimized transition state structures for the addition of HCl to acenes at the B3LYP/6-31G(d) level of theory (bond angles in deg and bond lengths in Å).

**TABLE 5: Calculated Activation Energies ($\Delta E_a$), Activation Free Energies ($\Delta G^{\ddagger}$), Product Energies ($\Delta E$), and Product Free Energies ($\Delta G°$) (kcal/mol, at B3LYP/6-3/G(d)+ZPVE, Relative to Water and Acene, Free Energies are calculated at 298 K) for the Addition of Water to Acenes[a]**

| | transition state | | product | |
|---|---|---|---|---|
| acene | $\Delta E_a$ | $\Delta G^{\neq}$ | $\Delta E$ | $\Delta G°$ |
| **1−1,4** | 71.1 | 79.8 | 24.5 | 32.3 |
| **2** | 63.2 | 73.5 | 13.6 | 22.9 |
| **3** | 53.2 | 63.4 | 0.9 | 10.6 |
| **4** | 49.2 | 58.6 | −2.5 | 6.4 |
| **5** | 44.7 | 54.6 | −10.5 | −1.1 |
| **6** | 43.4 (42.6) | 53.6 (52.0) | −10.7 (−11.4) | −0.9 (−2.5) |
| **7** | 43.0 (40.2) | 52.4 (49.6) | −11.6 (−14.3) | −2.7 (−5.5) |
| **8** | 44.3 (39.0) | 54.4 (49.2) | −10.5 (−15.7) | −0.8 (−6.0) |
| **9** | 45.5 (37.7) | 55.8 (47.1) | −9.3 (−17.2) | 0.5 (−8.3) |

[a] Reactions Involving **6−9** were calculated at UB3LYP/6-31G(d) (RB3LYP/6-31G(d) values are given in parentheses).

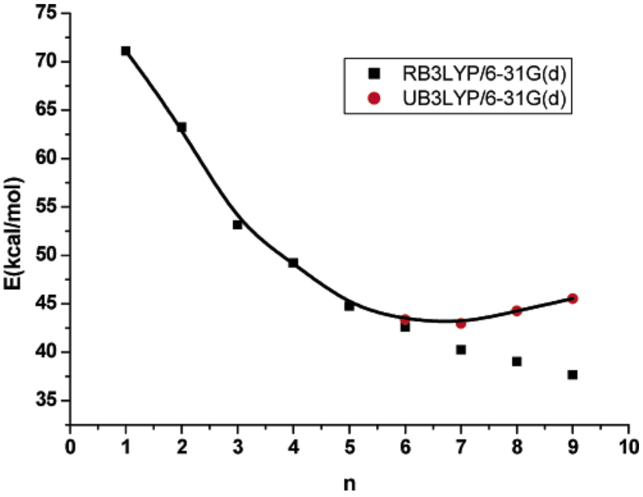


**FIGURE 8.** Activation energies for the addition of water to acenes, plotted as a function of annellation: (black square) at RB3LYP/6-31G(d) and (red circle) at UB3LYP/6-31G(d).

45.5 kcal/mol for longer acenes from pentacene to nonacene. For all transition states studied, the wave function for the addition of water to acenes is stable, in contrast to the wave function for transition states for the addition of HCl to longer acenes. Similarly to what occurs upon addition of HCl to acenes, the activation energy decreases as the number of benzene rings in the chain increases, from benzene (71.1 kcal/mol) to hexacene (43.4 kcal/mol), before staying nearly constant between hexacene (43.4 kcal/mol) and nonacene (45.5 kcal/mol) (referring to the UB3LYP/6-31G(d) results, Table 5, Figure 8). If RB3LYP/6-31G(d) values are considered, then an increase in the number of benzene rings is associated with a continuous reduction in the activation energy from benzene to nonacene (37.7 kcal/mol, Table 5, Figure 8). Even in the case of longer acenes, the activation barriers are still high and the reaction of acene with water is not expected to occur at room temperature or upon slight heating. Indeed, to the best of our knowledge, no uncatalyzed reactions between even longer acenes and water have been reported. We can conclude, based on the data in Table 5, that the reaction of pentacene with water is not expected to reduce the performance of pentacene-based organic electronic devices. As with the addition of HCl to acenes, the reactions of water with benzene, naphthalene, and anthracene are endothermic, while the reactions of higher acenes are exothermic.

Representative transition state structures for the addition of water to acenes are shown in Figure 9. All structures include a four-centered fragment involving the $C_\alpha$, $C_\beta$ of the central benzene ring, and the oxygen and $H^1$ of the water molecule. These four atoms are nearly in the same plane (the largest $H^1-O-C_\alpha-C_\beta$ dihedral angle is 0.6° for **2-H$_2$O-TS**). The TSs shown in Figure 9 indicate that the $C_\beta-H$ and $C_\alpha-OH$ bonds form synchronously. In contrast to HCl addition, the negative eigenvectors for the entire series of acenes studied show mostly that the $H^1$ hydrogen (i.e., the hydrogen that reacts with $C_\beta$) transfers from the oxygen to the acenes in the transition state, and that the motion of oxygen is negligible.[38] Analysis of the transition states indicates that those for the addition of water to acenes are “late” on the reaction coordinate. In the TSs, the $C_\beta \cdots H^1$ bond distances change significantly along the acenes series, increasing between **1-H$_2$O-1,4-TS** and **9-H$_2$O-TS** from 1.407 to 1.666 Å, while the $C_\alpha \cdots OH$ distances remain practically unchanged along the acenes series, ranging from 1.840 to 1.869 Å.[39] Thus, similarly to the addition of HCl to acenes, increasing

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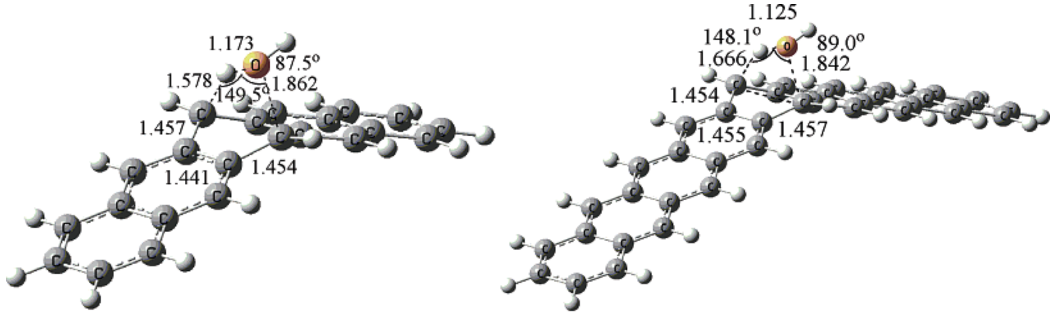
[38] A similar transition state was reported for water addition to silene and its nucleophilic−electrophilic nature was discussed in detail in: Bendikov, M.; Quadt, S. R.; Rabin, O.; Apeloig, Y. *Organometallics* **2002**, *21,* 3930.

[39] The respective $C_\beta \cdots H$ ($C_\alpha \cdots OH$) distances are the following: 1.407 Å (1.840 Å) in **1-H$_2$O-1,4-TS**, 1.433 Å (1.864 Å) in **2-H$_2$O-TS**, 1.503 Å (1.869 Å) in **3-H$_2$O-TS**, 1.533 Å (1.868 Å) in **4-H$_2$O-TS**, 1.578 Å (1.862 Å) in **5-H$_2$O-TS**, 1.601 Å (1.858 Å) in **6-H$_2$O-TS**, 1.628 Å (1.855 Å) in **7-H$_2$O-TS**, 1.648 Å (1.847 Å) in **8-H$_2$O-TS**, and 1.666 Å (1.842 Å) in **9-H$_2$O-TS**.



**5-$H_2O$-TS** **9-$H_2O$-TS**

**FIGURE 9.** Representative optimized TSs for the addition of water to acenes at the B3LYP/6-31G(d) level of theory (bond angles in deg and bond lengths in Å).

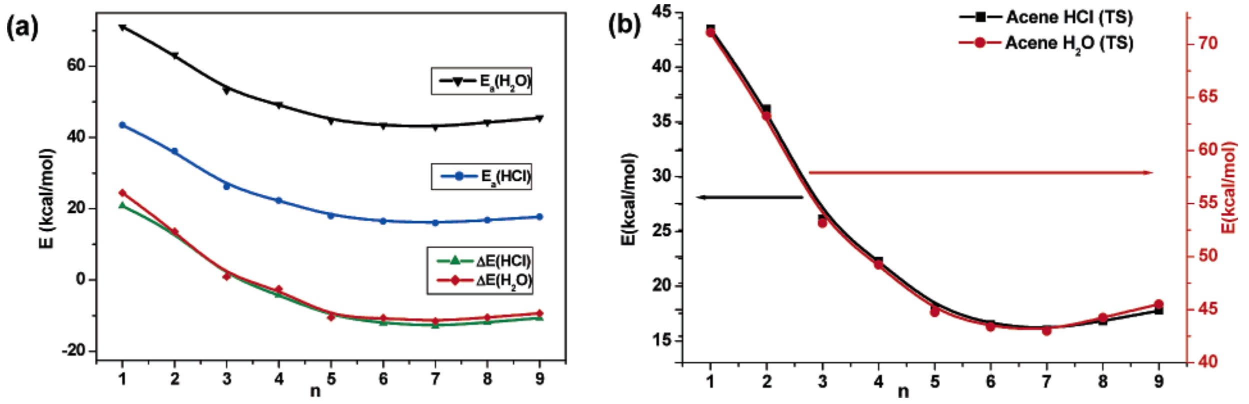


**FIGURE 10.** (a) Activation energies ($E_a$) and relative product energies ($\Delta E$) for the addition of HCl or water to acenes, plotted as a function of annellation (at RB3LYP/6-31G(d) for $n = 1-5$, at UB3LYP/6-31G(d) for $n = 6-9$). (b) Correlation between the calculated activation energies for the addition of HCl or water to acenes as a function of annellation: (black) addition of HCl to acenes; (red) addition of water to acenes (at RB3LYP/6-31G(d) for $n = 1-5$, at UB3LYP/6-31G(d) for $n = 6-9$). Right $y$-axis (which shows activation barriers for the addition of water) is shifted by 27 kcal/mol relative to the left $y$-axis (which shows activation barriers for the addition of HCl).

the number of benzene rings moves the transition state for the addition of water to acenes to an "earlier" point on the reaction coordinate. This correlates well with the exothermicity of the reaction, which increases as the number of benzene rings increases. For transition states, the wave function is stable for the addition of water to long acenes due to the relatively "late" character of those transition states compared to the transition states for the addition of HCl to acenes. This "lateness" leads to significantly greater bending of the acene skeleton in the transition state and to a decrease in the conjugation length in the transition state (Figure 9). In **5-$H_2O$-TS**, the sum of the angles around $C_\alpha$ is 352.5° and that around $C_\beta$ is 349.8°, while for **5-HCl-TS**, the sum of the angles around $C_\alpha$ is significantly larger, at 359.6°, while around $C_\beta$ it is smaller, at 344.9°. Thus, for HCl addition, the attack occurs mostly on $C_\beta$ while in the case of the addition of water, the attack occurs simultaneously on $C_\alpha$ and $C_\beta$.

**5. Comparison of Addition of HCl versus Water to Acenes.** Figure 10a compares the reaction energies for the addition of HCl to acenes with those for the addition of water. One of the interesting findings of this study is that the exothermicity of the HCl addition to acenes is very similar to the exothermicity of the water addition to acenes. Thus, according to the Hammond postulate, one can expect that the transition states for both reactions will also have similar energies. However, the activation energies for the addition of water are always ca. 27 kcal/mol higher than those for the addition of HCl (Figure 10b). HCl clearly acts as an electrophile in its addition to acenes, while the transition states for the addition of water to acenes show mostly a nucleophilic character with some electrophilic contribution, as shown by the direction of the negative eigenvector. Interestingly, the behavior of the activation energies as a function of the number of the benzene rings is practically the same (Figure 10a) for the addition of HCl (which is clearly electrophilic) and for the addition of water (which is mostly nucleophilic). Thus, we believe that the dependence of the activation energies (the shape of the curve in Figure 10b) on the number of benzene rings in the acene will be similar for other electrophiles and nucleophiles.

The activation energies for the addition of HCl and water decrease from benzene to hexacene. The current study shows that the activation barrier for the addition of HCl or water to higher acenes (from hexacene to nonacene) at UB3LYP/6-31G(d) remains almost constant (Figure 10a), thus longer acenes are as kinetically stable as hexacene. This is due to the ground state of the reactant (acenes) being stabilized by the contribution from the singlet biradical state.[16] Such a contribution is absent in the transition states for the addition of water and is small in the transition states for the addition of HCl.[35] At the RB3LYP/6-31G(d) level of theory, the kinetic stability of longer acenes decreases along the acene series. A similar trend is also observed for the exothermicity of these reactions (Figure 10a), which

**TABLE 6: Calculated Activation Energies ($\Delta E_a$), Activation Free Energies ($\Delta G^‡$), Product Energies ($\Delta E$), and Product Free Energies ($\Delta G°$) (kcal/mol, Relative to HCl or Water and Acene, Free Energies are Calculated at 298 K) for the Addition of HCl or Water to Substituted Acenes (at B3LYP/6-31G(d)+ZPVE)**

| | addition of HCl | | | | addition of water | | | |
|---|---|---|---|---|---|---|---|---|
| | transition state | | product | | transition state | | product | |
| substituted acene | $\Delta E_a$ | $\Delta G^‡$ | $\Delta E$ | $\Delta G°$ | $\Delta E_a$ | $\Delta G^‡$ | $\Delta E$ | $\Delta G°$ |
| 1-OMe | 34.9 | 43.4 | 26.2 | 34.8 | 70.0 | 78.8 | 21.8 | 30.5 |
| 1-H | 43.5 | 51.5 | 20.8 | 28.4 | 71.1 | 79.8 | 24.5 | 32.3 |
| 1-F | 48.4 | 57.0 | 21.5 | 29.9 | 76.3 | 85.4 | 21.4 | 30.0 |
| 1-CN | 50.8 | 60.4 | 22.9 | 32.0 | 61.3 | 71.6 | 19.0 | 28.2 |
| 3-OMe | 23.0 | 32.4 | 4.3 | 13.2 | 56.3 | 66.2 | 7.6 | 16.9 |
| 3-H | 26.2 | 35.6 | 1.0 | 10.3 | 53.2 | 63.4 | 0.9 | 10.6 |
| 3-F | 28.1 | 36.7 | 2.6 | 11.0 | 54.2 | 63.6 | 3.9 | 12.8 |
| 3-CN | 33.5 | 43.0 | 3.0 | 12.3 | 50.4 | 60.8 | 2.5 | 12.2 |
| 5-OMe | 16.2 | 24.6 | −8.0 | 0.5 | 46.9 | 56.2 | −5.9 | 3.0 |
| 5-H | 18.0 | 26.9 | −10.2 | −1.2 | 44.7 | 54.6 | −10.5 | −1.1 |
| 5-F | 19.5 | 28.4 | −9.3 | −0.3 | 45.1 | 54.9 | −8.2 | 1.2 |
| 5-CN | 24.0 | 32.9 | −8.3 | 0.7 | 43.4 | 53.3 | −8.3 | 1.0 |

increases from benzene to hexacene, and thereafter remains practically constant from hexacene to nonacene (at UB3LYP/6-31G(d)), since products do not receive a contribution from the singlet biradical state.[40] Thus, in contrast to previous expectations, and based on the significant increase in reactivity (and decrease in stability) found from benzene to pentacene, we predict that longer acenes (starting from heptacene) will be as stable (both kinetically and thermodynamically) as hexacene; however, the reactivity of the higher acenes toward electrophiles will be very high, which will preclude their isolation.[41]

**III. Addition of HCl or Water to Substituted Acenes.** Recently, several substituted tetracenes and pentacenes have been synthesized and tested in applications related to field effect transistors.[42] However, the relatively poor stability and solubility of acenes are major problems in their applications as organic semiconductors. Substituted acenes might be more environmentally stable and they are expected to be more soluble in organic solvents, which should allow investigation of their reactivity, and simplify their purification and processing. To explore the influence of donor and acceptor substituents on the kinetic and thermodynamic stability of acenes, we studied the model addition reactions of HCl and water to tetramethoxy-, tetrafluoro-, and tetracyano-substituted benzene (**1**), anthracene (**3**), and pentacene (**5**) (Scheme 2).

The calculated relative energies (at B3LYP/6-31G(d)) for the addition of HCl or water to the substituted acenes **1**, **3**, and **5** are given in Table 6. For comparative purposes, the equivalent data for the unsubstituted acenes are also given. In the case of HCl addition, substitution of acenes with electron-donating groups (such as OMe) lowers the activation barrier compared to that found for the unsubstituted acene, while substitution with electron-withdrawing groups (such as CN) raises the activation energy compared to that of the parent (unsubstituted) acene (Table 6), as expected for an electrophilic process. In the case of water addition, electron-donating groups increase the activation energy for addition to naphthalene and pentacene (but not to benzene), while electron-withdrawing groups lower it (Table 6), which is consistent with the mostly nucleophilic character of water addition to acenes. The effect of substituents on the activation energy depends on the length of the acene, spanning a range of 15.9, 10.5, and 7.8 kcal/mol for HCl addition to the OMe, F, and CN substituted **1**, **3**, and **5**, respectively, and spanning a range of 16.3, 5.9, and 3.5 kcal/mol for water addition to the OMe-, F-, and CN-substituted **1**, **3**, and **5**, respectively. For the discussion of the geometries of the substituted acenes see the Supporting Information.

In the case of substituted anthracenes and pentacenes, we have found good Hammett correlation between the calculated activation energies and the $\sigma_p$ of the substituents (Figure 11). The $\rho$ values[43] for the addition of HCl to anthracenes and pentacenes are −4.48 and −3.39, respectively, which clearly indicates an electrophilic mechanism with significant positive charge developing on the acenes in the transition states. The $\rho$ values for the addition of water to anthracenes and pentacenes are 2.35 and 1.39, respectively, which suggests a nucleophilic mechanism with some negative charge developing on the acenes in the transition states. The substituent effect is larger in the case of HCl than in the case of water. We note that in substituted pentacenes, the substituents are placed far away from the reaction center; however, calculated $\rho$ values are significant. Thus, electronic effects are transmitted very efficiently through the acene backbone. For the addition of water to acenes, the order of reactivity decreases in the order OMe > F > H > CN, which reasonably correlates with the $\sigma_p$ values for substituted anthracenes and pentacenes and with a nucleophilic addition mechanism (Table 6 and Figure 11). However, the activation barriers for tetrafluoro-substituted acenes are slightly higher than the activation barriers for the parent acenes, which is contrary

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[40] At the RB3LYP/6-31G(d) level of theory, the exothermicity of addition reactions continuously increases from benzene to nonacene (Tables 4 and 5).

[41] Other reactions, such as dimerization or reaction with oxygen, might also prevent isolation of longer acenes.

[42] (a) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin. S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482. (b) Meng, H.; Bendikov, M.; Mitchell, G.; Helgeson, R.; Wudl, F.; Bao, Z.; Siegrist, T.; Kloc, C.; Chen, C.-H. *Adv. Mater.* **2003**, *15*, 1090. (c) Sheraw, C. D.; Jackson, T. N.; Eaton, D. L.; Anthony, J. E. *Adv. Mater.* **2003**, *15*, 2009. (d) Moon, H.; Zeis, R.; Borkent, E.-J.; Besnard, C.; Lovinger, A. J.; Siegrist, T.; Kloc, C.; Bao, Z. *J. Am. Chem. Soc.* **2004**, *126*, 15322. (e) Swartz, C. R.; Parkin, S. R.; Bullock, J. E.; Anthony, J. E.; Mayer, A. C.; Malliaras, G. G. *Org. Lett.* **2005**, *7*, 3163. (f) Payne, M. M.; Parkin, S. R.; Anthony, J. E.; Kuo, C. C.; Jackson, T. N. *J. Am. Chem. Soc.* **2005**, *127*, 4986. (g) Jiang, J.; Kaafarani, B. R.; Neckers, D. C. *J. Org. Chem.* **2006**, *71*, 2155. (h) See ref 11.

[43] $\rho$ values were calculated at 25 °C by performing a linear regression on the data in Figure 11 for substituted anthracenes and pentacenes according to eq 1: $-\Delta E_a/RT = \sigma\rho$. An additive effect of 4 substituents was assumed ($^1/_4$ of the slope of the graphs in Figure 11 was used in eq 1). $\sigma_p$ values[3] were used for Figure 11 and eq 1 as the best available $\sigma$ values for molecules in Scheme 2.

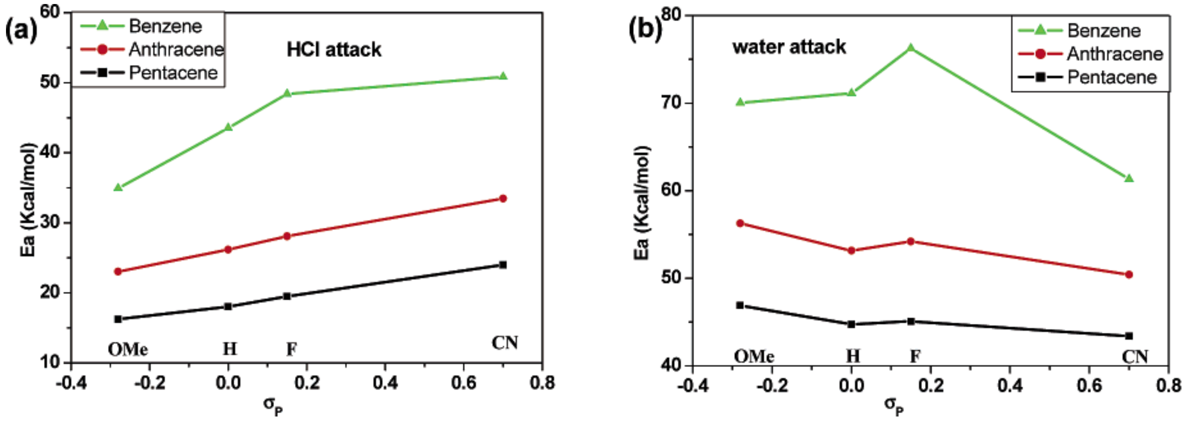

**FIGURE 11.** Relative activation energies for the addition of (a) HCl and (b) water to tetramethoxy-substituted (OMe), tetrafluoro-substituted (F), tetracyano-substituted (CN), and unsubstituted (H) benzene, anthracene, and pentacene, plotted as a function of $\sigma_p$.[3]

to what would be expected from the $\sigma_p$ value ($\sigma_p = 0.15$ for F)[3] and for a nucleophilic addition mechanism. We believe that this anomalous substituent effect of fluorine compared to methoxy and cyano substituents may be due to the fact that fluorine is a $\sigma$ electron acceptor and also a weak $\pi$ electron donor; however, in the case of anthracene and pentacene, the fluorine is placed far away from the reaction center, and electronic effects are very poorly transmitted through $\sigma$ bonds, while they are much better transmitted through $\pi$ bonds. Methoxy and cyano substituents are a $\pi$ electron donor and acceptor, respectively. We believe that $\rho$ values will be useful for the design of environmentally stable acenes for electronic applications, and also for predicting acene reactivity.

Electron-withdrawing substituents, such as CN, stabilize acenes, in general, and pentacene, in particular, toward electrophilic addition. For example, the activation energy barrier for the addition of HCl to the tetracyano-substituted pentacene lies between those of unsubstituted anthracene and tetracene. Thus, electron-withdrawing substituents should increase the environmental stability of pentacene-based organic electronic devices.[44] Water addition to acenes involves very high activation barriers and is not expected to play a role in acene decomposition, even for longer acenes. However, for nucleophilic addition, the energy barrier is smaller in the presence of electron-withdrawing substituents, as expected for a nucleophilic pathway.

## Conclusions

A systematic theoretical study of the addition of HCl and water to acenes was carried out. The activation energy barrier for the addition of water is very high compared to that for HCl addition (activation barriers for water addition are always higher by ca. 27 kcal/mol than the corresponding activation barriers for HCl additions), but the relative energies of the addition products are almost the same in both instances. HCl adds to acenes through a clearly electrophilic transition state, while water adds to acenes mostly through a nucleophilic transition state with some electrophilic character. The relative energies of the TSs for HCl and water addition show that the reactivity of the acenes increases as the number of fused benzene rings in the acene framework increases, up to hexacene. Interestingly, the reactivity of acenes from hexacene to nonacene remains almost constant.

A systematic study of the reactivity of substituted acenes predicts that the substituent effect will be large for HCl addition and smaller for water addition, and finds that the activation energies correlate linearly with $\sigma_p$. For example, the reactivity toward electrophiles of pentacene substituted with electron-withdrawing groups decreases significantly, and lies between the reactivities of unsubstituted anthracene and tetracene, providing an insight into the synthesis of environmentally stable pentacenes as well as longer acenes.

**Acknowledgment.** We dedicate this paper to Professor Zvi Rappoport (Hebrew University) on the occasion of his 70th birthday. We thank the MINERVA Foundation for financial support. M.B. is the incumbent of the Recanati career development chair and a member *ad personam* of the Lise Meitner-Minerva Center for Computational Quantum Chemistry.

**Supporting Information Available:** Reaction energies for the reactions of benzene and naphthalene with HCl and water at different theoretical levels; calculated solvent effect for addition of acenes to HCl; figures and discussion of optimized geometries for addition of HCl and water to substituted acenes; Mulliken and NPA charges for benzene−HCl and benzene−water complexes; and calculated absolute energies for all stationary points mentioned in the paper as well as the coordinates of their optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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[44] It is also known that pentacene substituted by electron-withdrawing groups is an n-type organic semiconductor. Sakamoto, Y.; Suzuki, T.; Kobayashi, M.; Gao, Y.; Fukai, Y.; Inoue, Y.; Sato, F.; Tokito, S. *J. Am. Chem. Soc.* **2004**, *126*, 8138.